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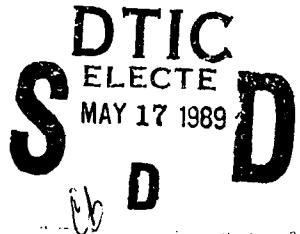
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UNIVERSITY OF NOTTINGHAM
DEPARTMENT OF CHEMISTRY

Corrosion of Aluminium Alloys by IRFNA

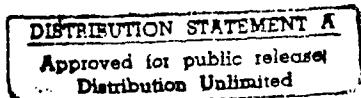
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19. ABSTRACT (Continue on reverse if necessary and identify by block number) It has been demonstrated electrochemically (by corrosion potential-time, polarization resistance and Tafel behavior) that the presence of a high concentration of Cu ²⁺ ions (580 wpm) in IRFNA (Inhibited Red fuming Nitric Acid) does not lead to an increase in the corrosion rate of aluminum alloy in this liquid oxidizer, or to any significant change in the corrosion potential of the system.					
The effect of the addition of water, to give an appreciably over-propellant specification level (6.75 wt.% H ₂ O), on the corrosion rate of aluminum alloy in IRFNA containing initially 2.79 wt.% H ₂ O has been investigated by corrosion potential-time polarization resistance and a.c. impedance measurements. The results indicate an order of magnitude increase in corrosion rate and an apparent increase in film thickness, following the addition of water.					
The effects of variations in IRFNA composition on the corrosion rate of aluminum alloy in IRFNA using four pairs of electrochemical cells, each pair containing IRFNA cont'd ...					
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obtained from a different source, have also been studied. The electrochemical results indicate that the alloy corrodes at a similar rate in IRFNA obtained from three different sources. Different behavior observed for the alloy in IRFNA from the fourth source is related to the high concentration of water in this IRFNA (4.45 wt.% on loading, 6.45 wt.% on recovery from, the electrochemical cell)

Auger electron spectroscopy has been used to monitor the effects of certain surface pre-treatments and exposure to IRFNA of samples of aluminum alloy. The washing of samples in water was found to produce an appreciable decrease in the thickness of the layer of corrosion products present on the sample surface. A gaseous fluorination procedure (HF/F_2 , 1 atmosphere, 24 hours), however, was found to have little effect on the composition and thickness of the film on the metal.

Analytical data has been obtained for the various samples of IRFNA used in the work described in the report.

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1) INTRODUCTION

This report presents the final phase of the work carried out under the revised agreements of March 1988 between Dr. Barry Allan (USAMC) and Drs. N.Logan and M.F.A.Dove (University of Nottingham, Department of Inorganic Chemistry).

The areas of investigation still outstanding or requiring completion after submission of the Second Interim Report (July 1988), are summarised below.

- A) The effect of dissolved Cu²⁺ ions and over-specification levels of water content on the corrosion rate of 2014 (3L65) aluminium alloy in IRFNA.
- B) The effects of variations in IRFNA composition on the corrosion rate of aluminium alloys in IRFNA (Electrolyte Effects).
- C) The effects of surface pretreatment and exposure to IRFNA of samples of 2014 (3L65) aluminium alloy using Auger Spectroscopy.

The work carried out under Part A is described and discussed in Section 2 (Effect of Cu²⁺ ions) and Section 3 (Effects of H₂O). Work carried out under Parts B and C are presented in Sections 4 and 5 respectively.

Further to these areas of research, analytical data has been obtained on IRFNA from the various sources used throughout

this work, and is presented in Section 6.

2) The Effect of Cu²⁺ on the Corrosion of 2014 (3L65)Aluminium Alloy in IRFNA2.1) Introduction

The corrosion of a pure metal in contact with an electrolyte depends upon the presence of anodic and cathodic sites on the metal surface. The anodic sites are usually associated with kink sites, dislocations and grain boundaries, with the cathodic sites making up the remainder of the surface.

The addition of alloying elements to improve the mechanical properties of metals may have a profound effect on the corrosion resistance of these metals, due to the formation of galvanic couples.

The galvanic couple between dissimilar metals can be treated by the application of mixed-potential theory. For instance, when a piece of platinum is coupled to a piece of zinc in an air-free acid solution, vigorous hydrogen evolution occurs on the surface of the platinum and the rate of hydrogen evolution on the zinc is decreased. Furthermore the rate of dissolution of the zinc (the corrosion reaction) increases. The increase in corrosion rate of the zinc in this example is due to higher exchange-current density for hydrogen evolution on platinum surfaces.

Another important factor in galvanic corrosion is the area effect, or the ratio of cathodic to anodic areas. For a given current flow in the cell, the current density at a small electrode

will be greater than that at a large electrode. Thus, if the more noble metal in a galvanic couple is present as a larger surface area than the more active metal, the corrosion current density at the active metal will be high and thus the metal will corrode at a high rate. To summarise, an unfavourable area ratio consists of a large cathode and a small anode.

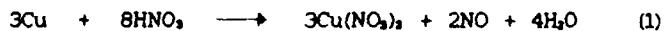
Since copper ions are known to be reduced by aluminium in aqueous acid solutions to produce elemental copper, there exists the possibility that reduced copper would "plate-out" upon the surface of aluminium and its alloys, producing cathodic sites for the reduction of NO_3^- , and thus increasing the rate of corrosion of the aluminium metal. Furthermore, the presence of the intermetallic compound CuAl_2 may produce local galvanic cells on the alloy surface in which the aluminium becomes the active anodic sites. This behaviour has been reported elsewhere.¹

With these considerations in mind, the effect of the addition of Cu^{2+} ions on the corrosion rate of 2014 (3L65) aluminium alloy in IRFNA has been investigated.

2.2) Experimental

2.2.1) Preparation of Cu²⁺/RFNA solution

In order to study the effect of the addition of Cu²⁺ ions to the corroding aluminium alloy system, a solution of Cu²⁺ ions in RFNA was prepared. Copper wire (ca. 1.75g, abraded) was placed in a "quickfit" tube containing RFNA. Moisture was prevented from entering the tube during transfers of materials by a stream of dry nitrogen. A P.O. guard tube was fitted to the "quickfit" tube, and the apparatus was left to stand at room temperature until no further reaction could be seen to be taking place. Within a few minutes of adding the wire, a green colouration was observed. Over a period of several days the colour of the solution darkened and deep blue crystals were formed both in the bottom of the tube, and on the metal surface. The familiar equation for the reaction between copper metal and nitric acid is shown below (1):



Prior to removing the solution for injection into an electrochemical cell, the copper concentration was determined by AAS to be 1.005 wt.% and its density was determined as 1.642g cm⁻³.

2.2.2) Introduction of Cu²⁺/RFNA solution into an electrochemical cell

Under a counter-current of dry nitrogen, the Cu²⁺/RFNA solution was drawn into a 1cm³ glass-bodied syringe (Weber Scientific, England). 0.5 cm³ of the solution was injected through the Teflon reference electrode seat of cell AF058/2. The platinum reference electrode wire had previously been removed to facilitate this operation. After withdrawing the syringe, a Teflon disc was placed over the electrode seat and compressed into place by the brass nut, sealing the cell from ingress of moisture or loss of electrolyte.

Given that cell AF058/2 was initially filled with 13.403g IRFNA, the addition of 0.5cm³ of a 0.0165g Cu²⁺cm⁻³ RFNA solution produced a final copper concentration in the cell of 8.25mg Cu²⁺/ 14.224g electrolyte (580 wppm Cu²⁺).

2.2.3) Electrochemical Investigation

Prior to the introduction of the Cu²⁺/RFNA solution into the cell, routine measurements were made on E_{corr} and R_{ct}. Immediately after addition of the Cu²⁺/RFNA solution, further measurements were taken. The results are displayed graphically in Figures 1 and 2.

In order to assess the effects of any "plated-out" copper on the corrosion process, Tafel polarisations were carried out on this system and, for direct comparison, on the complementary cell

AF058/1, which had received no addition of Cu²⁺ ions.

2.2.4) Analysis of Electrolyte

At the end of the test period, the cell AF058/2 was opened and the electrolyte removed for the determination of dissolved metals content (aluminium and copper), HF content and water content. The results of these analyses are presented in Section 2.3.4.

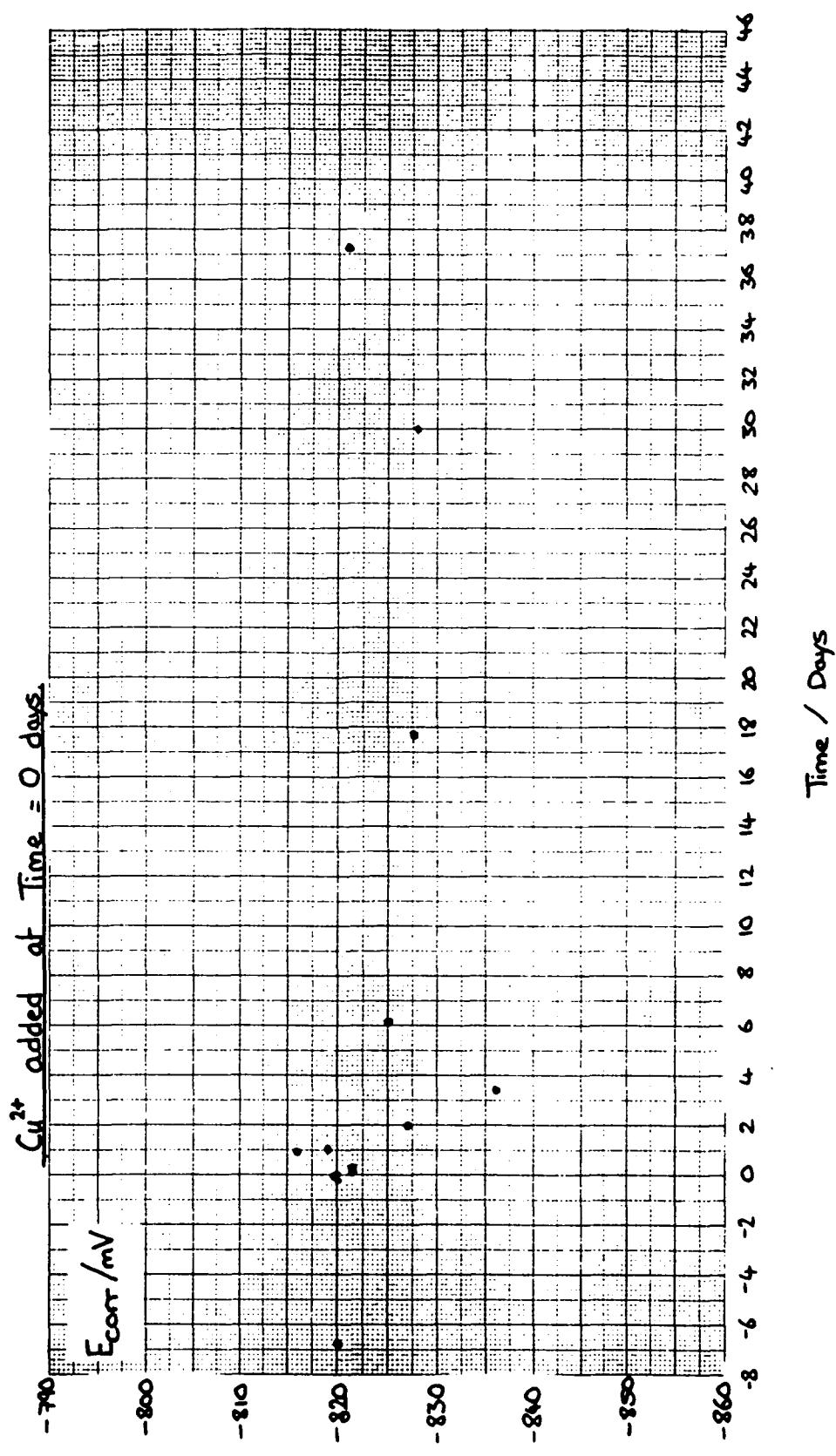
2.3) Experimental Results

2.3.1) E_{corr} - Time behaviour

Figure 1 shows the E_{corr} versus time behaviour of cell AF058/2 before and after the addition of the Cu²⁺/RFNA solution.

Clearly, although a small perturbation in the corrosion potential was observed immediately on injecting the copper solution into the electrochemical cell, the corrosion potential did not undergo its greatest change until some 24 hours after injection, when the potential rose from a value of -823mV (versus the NO₃⁻/N₂O₄ couple) to -816mV and then fell to a value of -837mV. After a further five days, the corrosion potential fluctuated within the range -825mV to -836mV, and then stabilized at -828mV. After a period of ca. 46 days the corrosion potential had increased to -821mV, only 1mV lower than the value

Figure 1 The effect of Cu^{2+} addition on the corrosion potential (E_{corr}) of 2014 (3165) Aluminium alloy in IRFNA. Cell AF058/2



recorded seven days prior to the addition of the copper solution.

2.3.2) Polarisation-Resistance behaviour

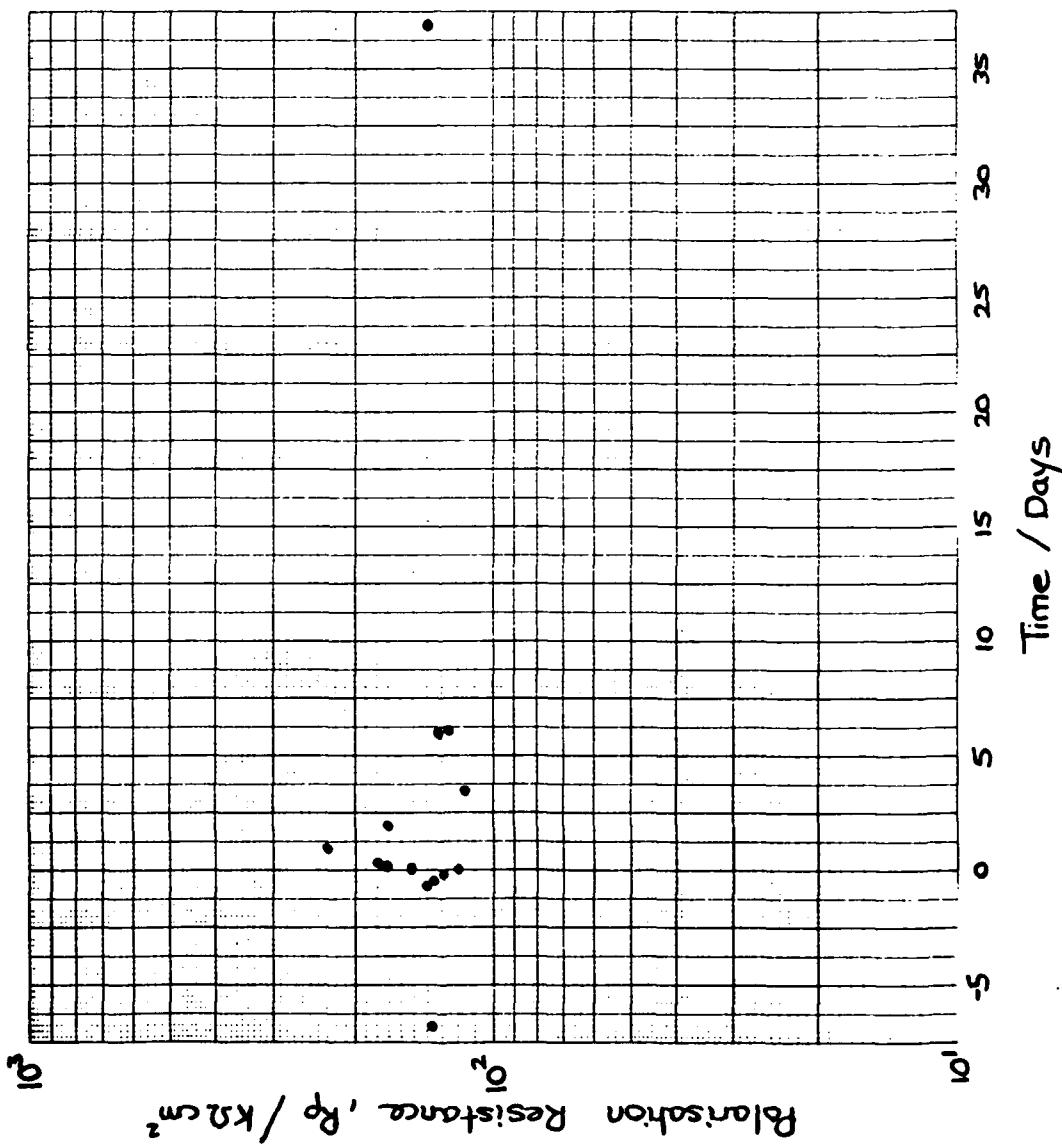
The prime concern during this study has been the effect of Cu^{2+} ions in IRFNA upon the corrosion rate of the 2014 (3L65) aluminium alloy. A series of polarisation experiments has therefore been conducted, from which values of the polarisation resistance, R_p , have been obtained. This parameter is inversely proportional to the corrosion rate. Figure 2 shows the R_p -time behaviour of the cell AF058/2 before and after addition of Cu^{2+} ions to the system.

The addition of the Cu^{2+} ions was made at time $T=0$ days (Figure 2). In the six day period following the addition of the Cu^{2+} ions, R_p can be seen to have increased, indicating a decrease in corrosion rate, and then decreased, corresponding to an increase in corrosion rate. The value of R_p recorded after ca. 6 days (ca. $125\text{k}\Omega \text{ cm}^2$) is very similar to values recorded ca. 7 days before addition of Cu^{2+} ions ($137.7\text{k}\Omega \text{ cm}^2$), and ca. 37 days after Cu^{2+} ion addition ($140.9\text{k}\Omega \text{ cm}^2$).

2.3.3) Tafel behaviour

Corrosion current densities of AF058/2 (after addition of Cu^{2+} ions) and AF058/1 (no added Cu^{2+} ions) were obtained directly from data obtained by the Tafel polarisation method. At ca. 1 day after addition of copper to AF058/2, the corrosion

Figure 2
 Effect of Cu^{2+} addition on
 the Polarisation Resistance,
 R_p , of 2011₄ (3L65)
 Aluminium alloy in IRNA.
 cell AFO58/2. Cu^{2+} added
 at T=0 days.



current density, i_{corr} , was measured as $2.5 \times 10^{-7} \text{ A cm}^{-2}$.

After 3.42 days, i_{corr} was measured as $4.9 \times 10^{-7} \text{ A cm}^{-2}$.

These values are similar to the value obtained from cell AF058/1,

$7 \times 10^{-7} \text{ A cm}^{-2}$, after a similar time.

2.3.4) Analytical Results

The results of analyses carried out on AF058 "stock" IRFNA and IRFNA removed from the two AF058 electrochemical cells are presented below in Table 2.1.

Table 2.1 Analytical Data for AF058 cells

	Al /ppm	Cu /ppm	Fe /ppm	Cr /ppm	Ni /ppm	HF /wt%	H ₂ O /wt%	TDS /wt%
AF058 (stock)	205	1.1	6.8	1.7	ND	0.503	2.839	0.043
AF058/1	325.4	4.6	-	-	-	0.355	3.077	-
AF058/2	169	816.4	-	-	-	0.401	3.503	-

2.4) Conclusions

It was proposed that the presence of copper ions in sufficiently high concentrations in these systems might lead to a "plating-out" effect of metallic copper on the surface of the aluminium alloy. This would provide an increased surface area upon which the cathodic reduction reaction could take place:



The increased cathodic current would be balanced by an increased anodic current, corresponding to an increased corrosion rate of the aluminium alloy. A shift in E_{corr} would also be expected as the system took up the potential of the mixed couple between copper and the aluminium alloy.

The electrochemical results presented in Sections 2.3.1, 2.3.2 and 2.3.3 indicate that the presence of a high concentration of Cu^{2+} ions in the electrolyte does not lead to an increase in corrosion rate of the aluminium alloy, or to any significant change in the corrosion potential of the system.

The results of analyses carried out on the electrolyte recovered from the cells are not easy to interpret (Table 2.1). Both cells showed an increase in water content of the recovered electrolyte, consistent with the corrosion process. However, AF058/2 showed an aluminium content (169 ppm) lower than that measured for the "stock" AF058 IRFNA (205 ppm). Acid recovered from AF058/1 had an aluminium content (325.4 ppm) more consistent with a system which had been corroding for some time. The very high level of copper measured in AF058/2 is inconsistent with the amount of copper added to the cell (0.5cm³ of a 0.0165gCu²⁺/cm³ solution) to give the calculated 580ppm concentration. This inconsistency may be explained in either of two ways:

- 1) After injection of the Cu²⁺/RFNA solution into the cell, the cell was not effectively sealed, allowing electrolyte to escape from the cell. This would have lead to partial dissolution

of the brass nut and incorporation of the copper from this dissolution process into the bulk electrolyte within the cell, thereby increasing the Cu^{2+} concentration above the level calculated.

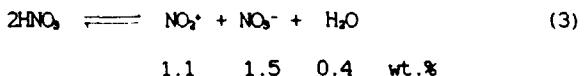
2) A small quantity of particulate copper nitrate may have been inadvertently injected into the cell with the Cu^{2+} /RFNA solution, resulting in a copper concentration in excess of that calculated.

It is unlikely that the presence of Cu^{2+} ions above the level expected (based upon the amount of Cu^{2+} /RFNA solution injected into the cell) could be due to the dissolution of copper from the bulk aluminium alloy.

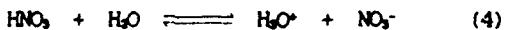
3) The Effect of Over-Specification Levels of Water Content on
the Corrosion Rate of 2014(3L65) Aluminium Alloy in IRFNA

3.1) Introduction

The chemistry of 100% nitric acid is governed by the self-dissociation equilibrium (3):



Solvation of the water and nitrate ions by nitric acid is strong³. Clearly, addition of one of the components on the right hand side of equilibrium (3) is expected to suppress the concentrations of the other two. For instance, the addition of water is seen to reduce the conductivity of the nitric acid as the concentrations of NO_3^+ and NO_3^- are reduced^{3,4}. A conductivity minimum is observed at ca. 4 wt.% water, and the increase in conductivity with further water additions is attributed to the production of the hydroxonium ion, according to (4):



In the event of (4) occurring in the aluminium alloy - IRFNA system, it would be reasonable to assume that reduction of

the hydroxonium ion (H_3O^+) might be the predominant cathodic process accompanying the anodic oxidation of the metal.

The current density for the reduction of hydroxonium ion on the aluminium alloy is greater than the corresponding current density for the reduction of nitronium ions, and so the corrosion rate of the metal is also greater.

In view of the importance of this effect, the corrosion rate of the aluminium alloy in IRFNA "doped" with water to a level considerably in excess of that recommended by the current IRFNA specification⁶, has been investigated.

3.2) Experimental

3.2.1) Electrochemical Cell Selection

In order to obtain corrosion rate measurements which reflect the effect of the addition of water to an electrochemical cell, it was decided to utilise a cell which had been set up for a period of time greater than the ca. 80 day induction period normally required for equilibrium in these systems⁶.

Cell BW19 was selected for this purpose. This cell was originally set up on 11/9/86, and filled with 11.768g of "new" Westcott IRFNA. The cell had been pretreated with aqueous HF(0.05% aqueous solution), and gaseous ClF₃ (1 atm., RT, 17hrs).

A series of polarisation experiments was carried out on BW19 prior to the addition of water. Similarly, ac-impedance

spectra were recorded over the frequency range 10^4 to 10^6 Hz, from which the capacitance of the oxide/fluoride film present on the metal surface could be determined. Any changes in this parameter, resulting from the addition of water to the cell, could thus be observed.

3.2.2) Introduction of H₂O to cell BW19

The removal of the platinum reference electrode wire from the cell provided an injection port through which 0.5g "nanopure" H₂O (0.5 cm³) was injected into the cell, using a 1cm³ glass-bodied syringe. The final concentration of water in the cell was calculated to be 6.75wt%. Immediately after withdrawal of the syringe needle, a PTFE disc was placed over the electrode seat and compressed into place by the brass bolt, thus forming an effective barrier against loss of electrolyte from the cell, or ingress of moisture into the cell.

3.2.3) Electrochemical Investigation

Following the addition of water to the electrochemical cell, electrode potential, E_{corr}, polarisation resistance, R_p, and film capacitance, C, were measured. The results are displayed graphically in Figures 3, 4 and 5.

3.3) Experimental Results

3.3.1) E_{corr} - Time behaviour

Figure 3 displays the effect of water addition on the

corrosion potential of BW19. Prior to the addition of water to the cell, values of the corrosion potential, E_{corr} , were recorded between -808mV and -820mV. Immediately on adding water (T=0 days), E_{corr} was seen to increase to a value of -732mV. Within 24 hours, however, the corrosion potential had fallen to a level of -827mV. The potential then increased steadily over a period of ca. 24 hours to -776mV. E_{corr} remained at between -780mV and -794mV over the following ten days, after which the cell was dismantled.

3.3.2) Polarisation-Resistance behaviour

The effect of water addition on the polarisation resistance of BW19 is displayed in Figure 4.

Clearly, the addition of water, shown as occurring at time T=0 days, reduces the polarisation resistance by an order of magnitude, resulting in a ten-fold increase in corrosion rate. Over the period of study, ca. 12 days after water addition, the polarisation resistance had not returned to its pre-addition level. The final value before dismantling the cell was determined as $49.14\text{k}\Omega\text{cm}^2$.

3.3.3) Film Capacitance - Time behaviour

Figure 5 shows the change in capacitance of the system with time as a result of the addition of water. Clearly, a decrease in capacitance from ca. $4.5\mu\text{Fcm}^{-2}$ to ca. $3.2\mu\text{Fcm}^{-2}$ is observed over the three day period following water addition.

Figure 3

The effect of water addition on the Corrosion Potential E_{corr} of
2014 (316S) Aluminium alloy in IRFNA. Cell BW19.
Water added at 0 days.

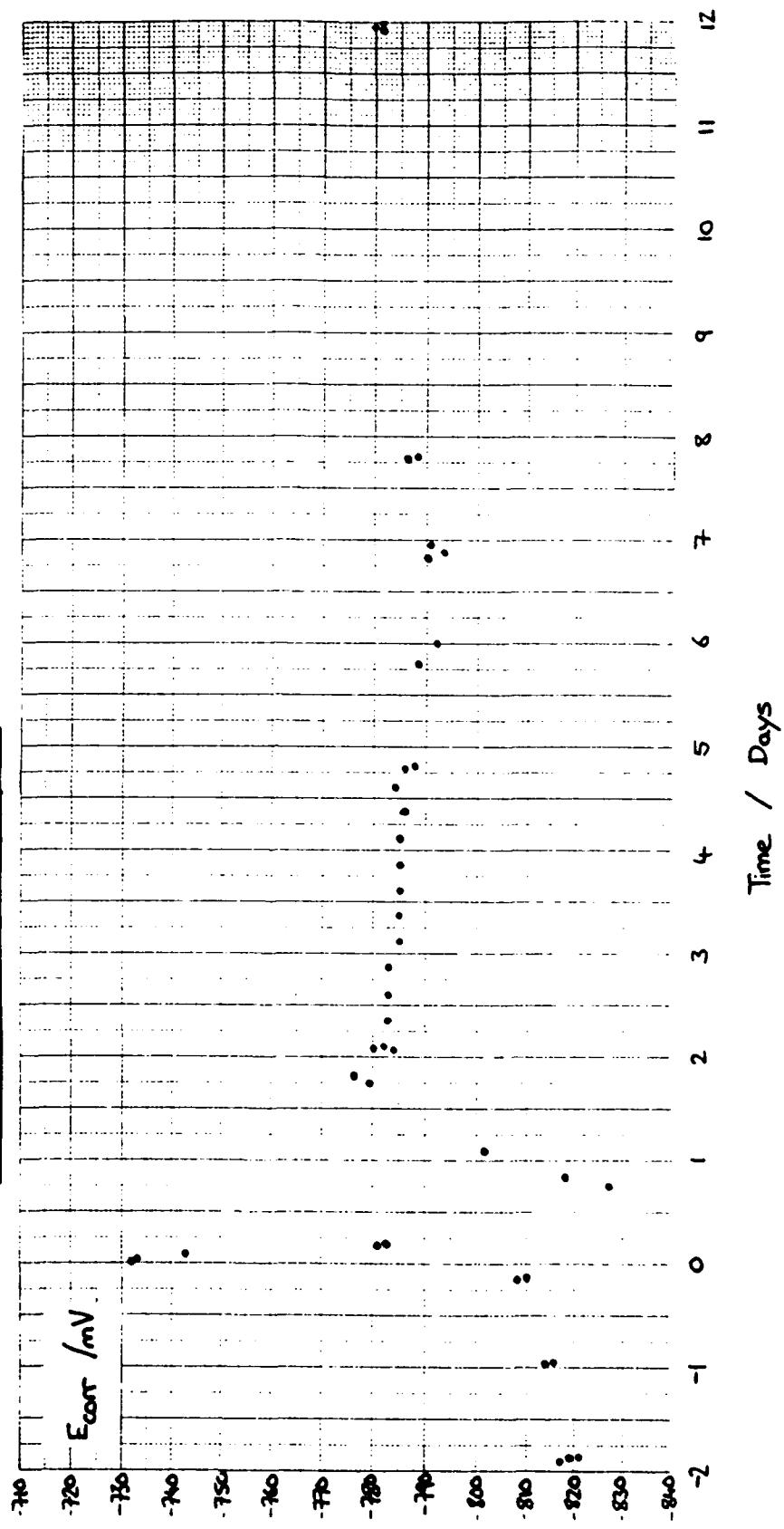


Figure 4

The effect of water addition
on the Polarisation Resistance
of 2014 (3L65) Aluminium
alloy in IRFNA. Cell 8W19
Water injected at 0 days.
Electrode area = 1.767 cm^2
DC Polarisation data (•)
AC Impedance data (+)

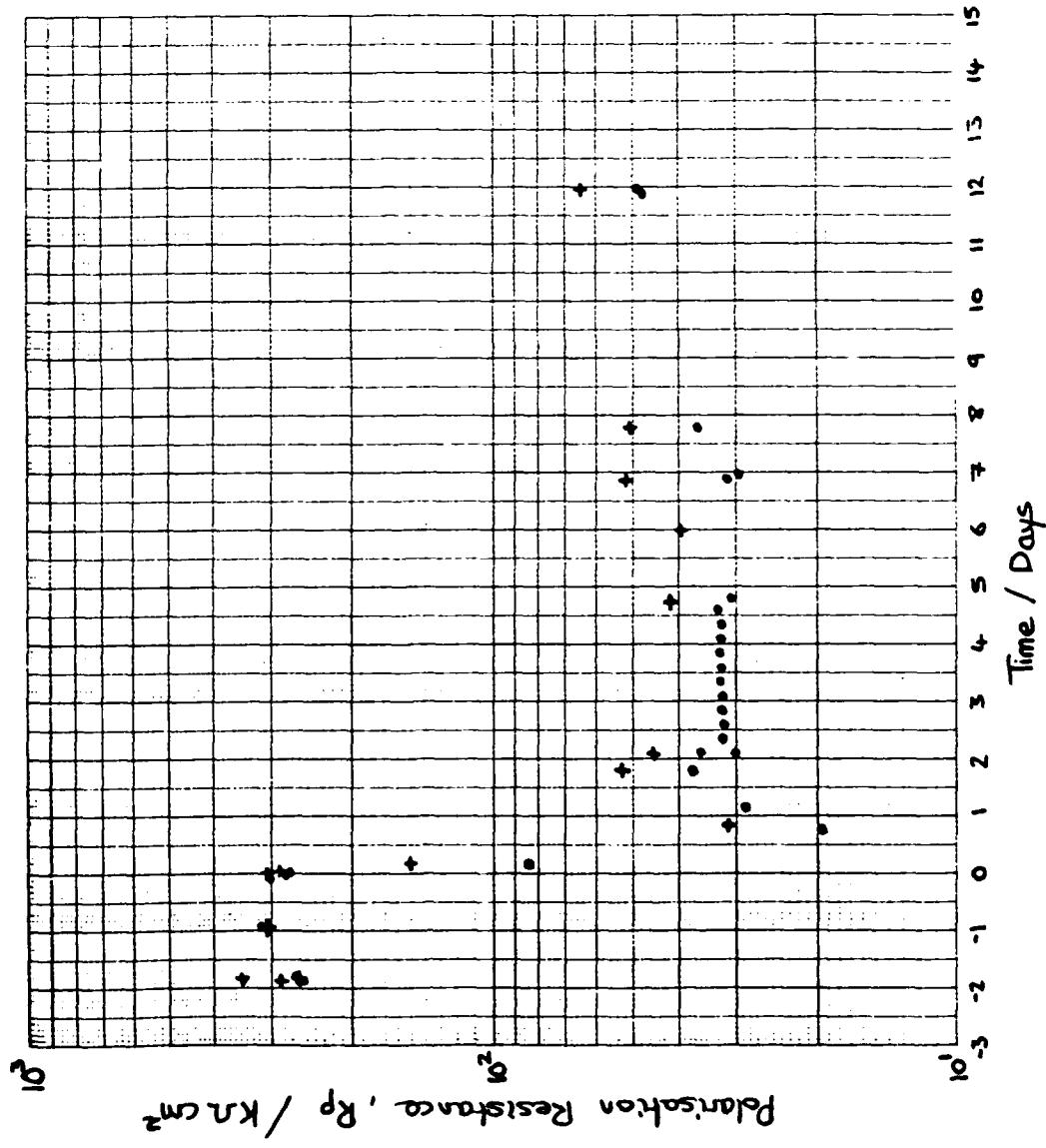
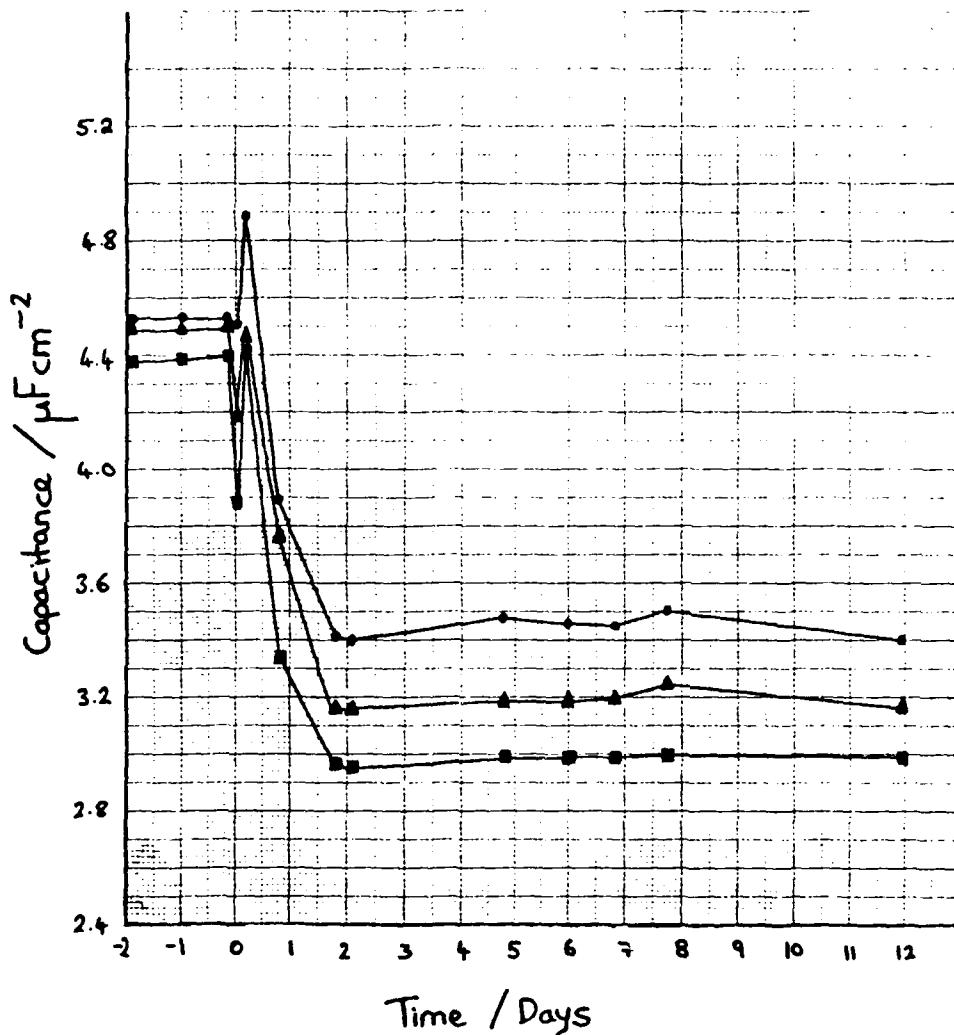


Figure 5 The effect of Water addition on the capacitance of the oxide/fluoride film on 2014 (3L65) Aluminium alloy in IRFNA



Capacitance measured at 10 Hz. (○)
100 Hz (□)
1000 Hz (■)

3.3.4) Analytical Results

Following the completion of electrochemical tests on this system, the cell BW19 was taken off-test and opened. The acid electrolyte was removed in the usual manner and stored in a screw-capped FEP bottle.

The electrolyte was analysed for fluoride ion content (fluoride ion electrode), and the HF content determined as <0.064 wt% .

3.4) Conclusions

The corrosion potential-time data, displayed graphically in Figure 3, show that the addition of 0.5g water to an equilibrated aluminium /IRFNA system (of initial $[H_2O] = 2.79$ wt.%) causes a rapid increase in potential, followed by a decrease and a further increase to potentials very close to pre-water addition levels. These sharp fluctuations in potential may occur as a result of:

- i) Physical disturbance of electrode surfaces during the water injection process.
- ii) Release of heat of dilution on addition of water
- iii) Establishment of a new cathodic process at the metal-film or film-electrolyte interface.

The increase in corrosion current density associated with a decrease of polarisation resistance, R_p , after addition of

water, is of the order of a ten-fold increase. This increase is expected to produce a build-up of corrosion products at the working electrode surface, leading to film thickening. The increase in film thickness corresponds to the observed decrease in the capacitance of the film as determined from AC impedance data. The exchange of hydroxyl groups, in the hydrated oxide/fluoride film present on the alloy surface, by fluoride ions, will result in a decreased fluoride ion content and an increase in the water content of the electrolyte.

The low concentration of fluoride ions in the electrolyte removed from the cell at the end of the test period (<0.064 wt%), is consistent with the increased corrosion rate observed. Clearly, this level of corrosion is undesirable and results from the high level of water present in the electrolyte (ca. 6.75 wt.% H₂O).

4) Electrolyte Effects

4.1) Experimental

In order to assess the effects of variations in IRFNA composition on the corrosion rate of 2014 (3L65) aluminium alloy in IRFNA, four pairs of cells were machined from 3L65 alloy, each containing "bottom working electrodes" cut from SN5144 oxidiser tank wall section. Each pair of cells was filled with IRFNA obtained from different sources. The cells were thermostatted in an oil bath maintained at 25°C. The corrosion potential, E_{corr} , and polarisation resistance, R_p , were measured intermittently.

These cells were taken off test on February 7, 1989, and the acid electrolyte removed for analysis (Section 4.2.4). Visual inspections of the cell interiors were made. The results of these inspections are reported below (Section 4.2.3).

Table 4.1 shows cell codes, IRFNA type and set-up dates for the four pairs of electrochemical cells.

Table 4.1 Electrochemical Cell Data

<u>Cell Code</u>	<u>IRFNA Type</u>	<u>Weight of IRFNA/g</u>	<u>Set-up date</u>
Boom 1	Boom	13.728	13-4-88
Boom 2	Boom	12.069	14-4-88
AF058/1	AF058	13.454	28-4-88
AF058/2	AF058	13.403	28-4-88
SN5208/1	SN5208	13.943	20-5-88
SN5208/2	SN5208	14.398	20-5-88
W1	Westcott	12.141	20-6-88
W2	Lot 67 Dr. 3	13.972	24-6-88

4.2) Experimental Results4.2.1) E_{corr} -Time behaviour

Figures 6, 7, 8 and 9 display the corrosion potentials of the four pairs of electrochemical cells as a function of time.

As reported previously⁹, the potential-time behaviour of three of the four pairs of electrochemical cells is typical for fluoride film covered aluminium alloys in contact with IRFNA. These three pairs of cells (W1, W2, SN5208/1, SN5208/2, Boom1 and Boom2) show a fall of electrode potential to ca. -820mV after a period of 50 days or less (Figures 7,8 and 9). In the case of the SN5208 pair of cells, this fall in potential to a steady value was seen to occur within five days of the cell being set up (Figure 7). The results obtained for the AF058 pair of cells (Figure 6) show markedly different behaviour. Particularly noticeable is the slow rate of fall of electrode potential with time for both cells. After 50 days, the electrode potentials of AF058/1 and AF058/2 were

Figure 6 : E_{corr} vs. Time AF058/1 (●) AF058/2 (▲)

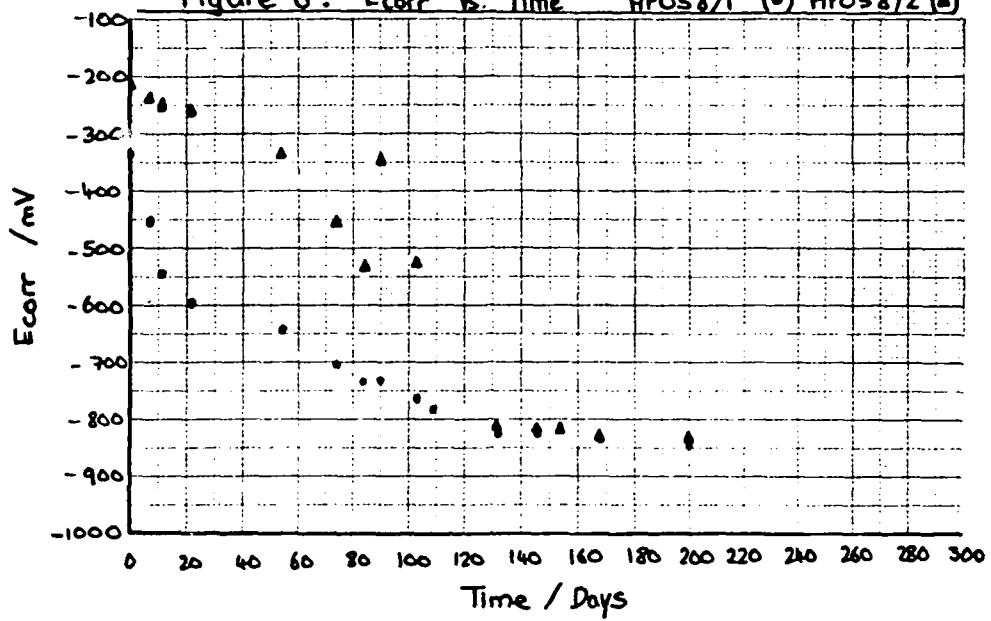


Figure 7 : E_{corr} vs. Time SNS208/1 (●) SNS208/2 (▲)

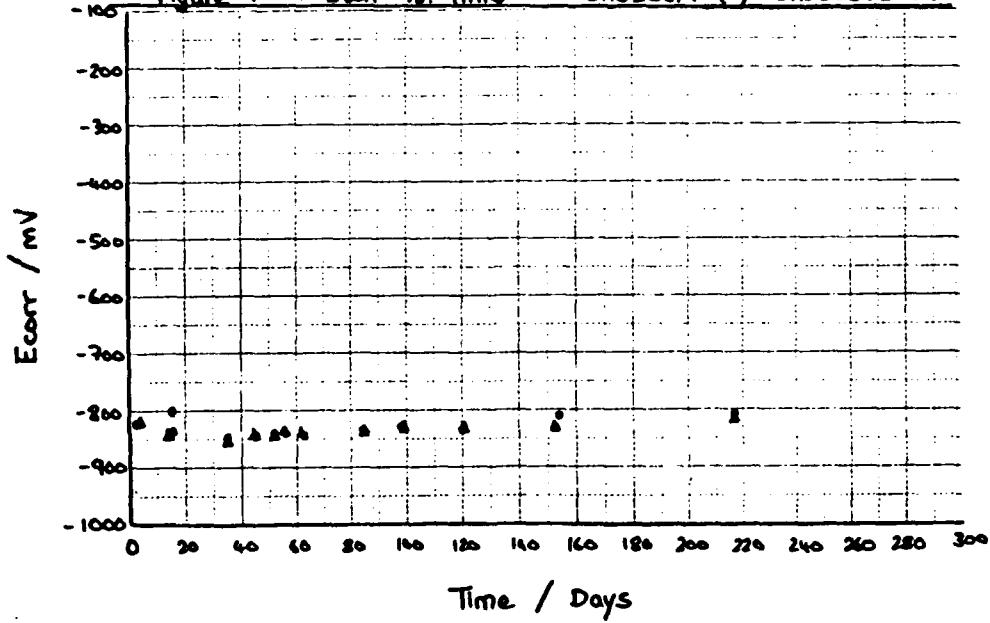


Figure 8. E_{corr} vs. Time

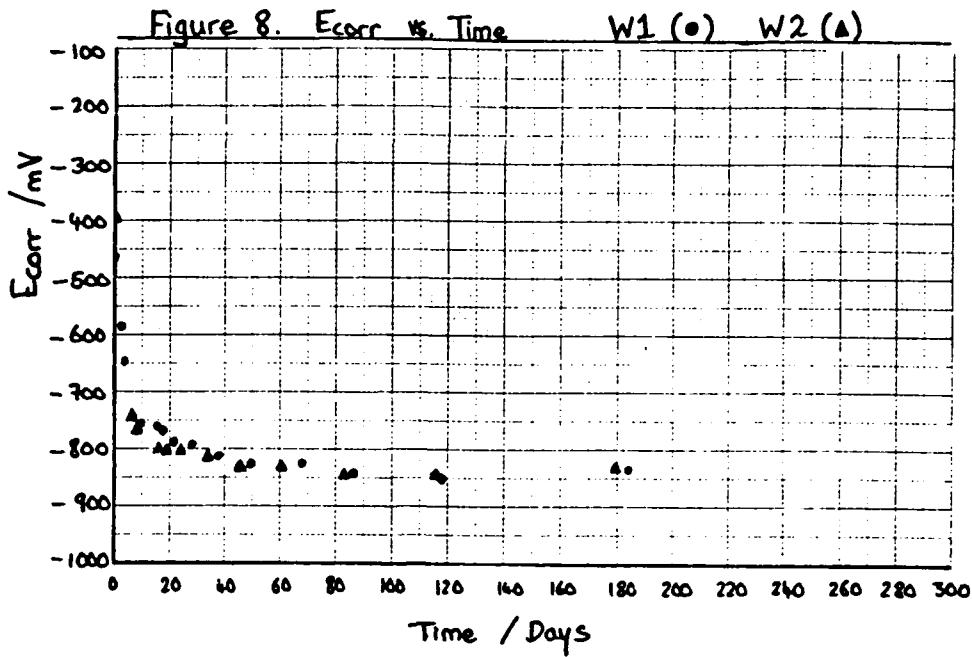
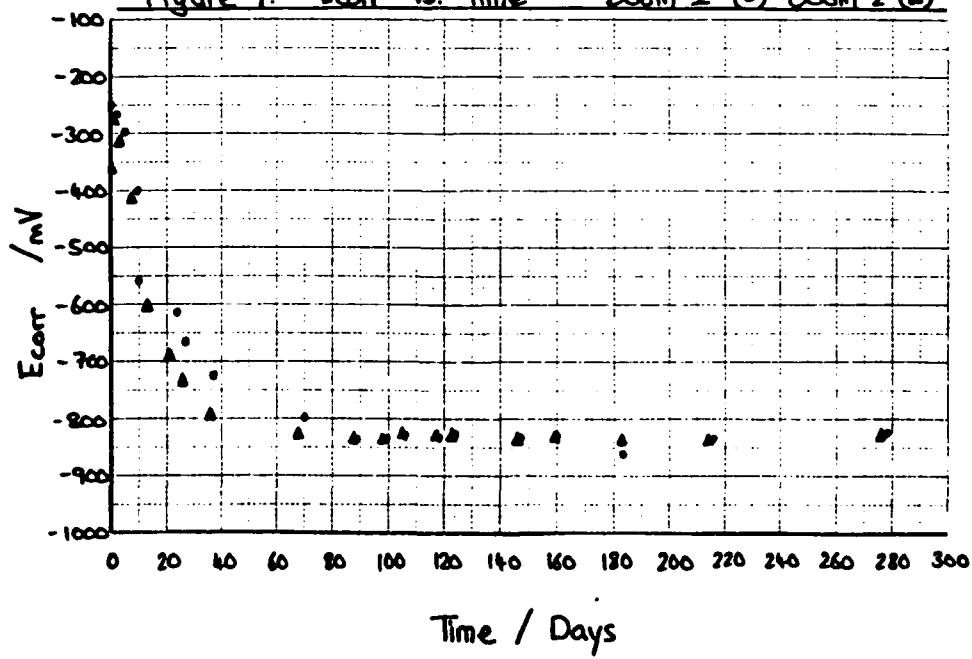


Figure 9. E_{corr} vs. Time Boom 1 (○) Boom 2 (△)



ca. -640mV and -335mV respectively. This slow rate of fall in potential is more typical of untreated 3L65 aluminium alloy when exposed to IRFNA. Also noticeable is the difference in potential-time behaviour of the two AF058 cells. Since both cells contain IRFNA from the same source, working electrodes cut from the same area of oxidiser tank wall section, and have both experienced the same temperature environment etc., this type of behaviour is untypical.

4.2.2) R_p - Time behaviour

Figures 10 to 13 show the polarisation resistance - time behaviour of the four pairs of electrochemical cells. Since the relationship between polarisation resistance, R_p , and corrosion current density, i_{corr} , is a reciprocal one, a decrease in R_p corresponds to an increase in corrosion rate.

Although all four pairs of cells show an initial decrease in polarisation resistance, obvious differences between pairs of cells can be seen. A comparison of the results obtained from the SN5208 pair of cells (Figure 11), with those obtained from cells containing AF058, Westcott and Boom electrolytes (Figures 10, 12 and 13), shows that after ca. 60 days, the polarisation resistance of the SN5208 cells increases sharply, whereas the results obtained from the other cells indicate a continued decrease in R_p , corresponding to an increase in corrosion rate. This anomalous

Figure 10
 R_p versus Time
AF058/1 (•)
AF058/2 (▲)

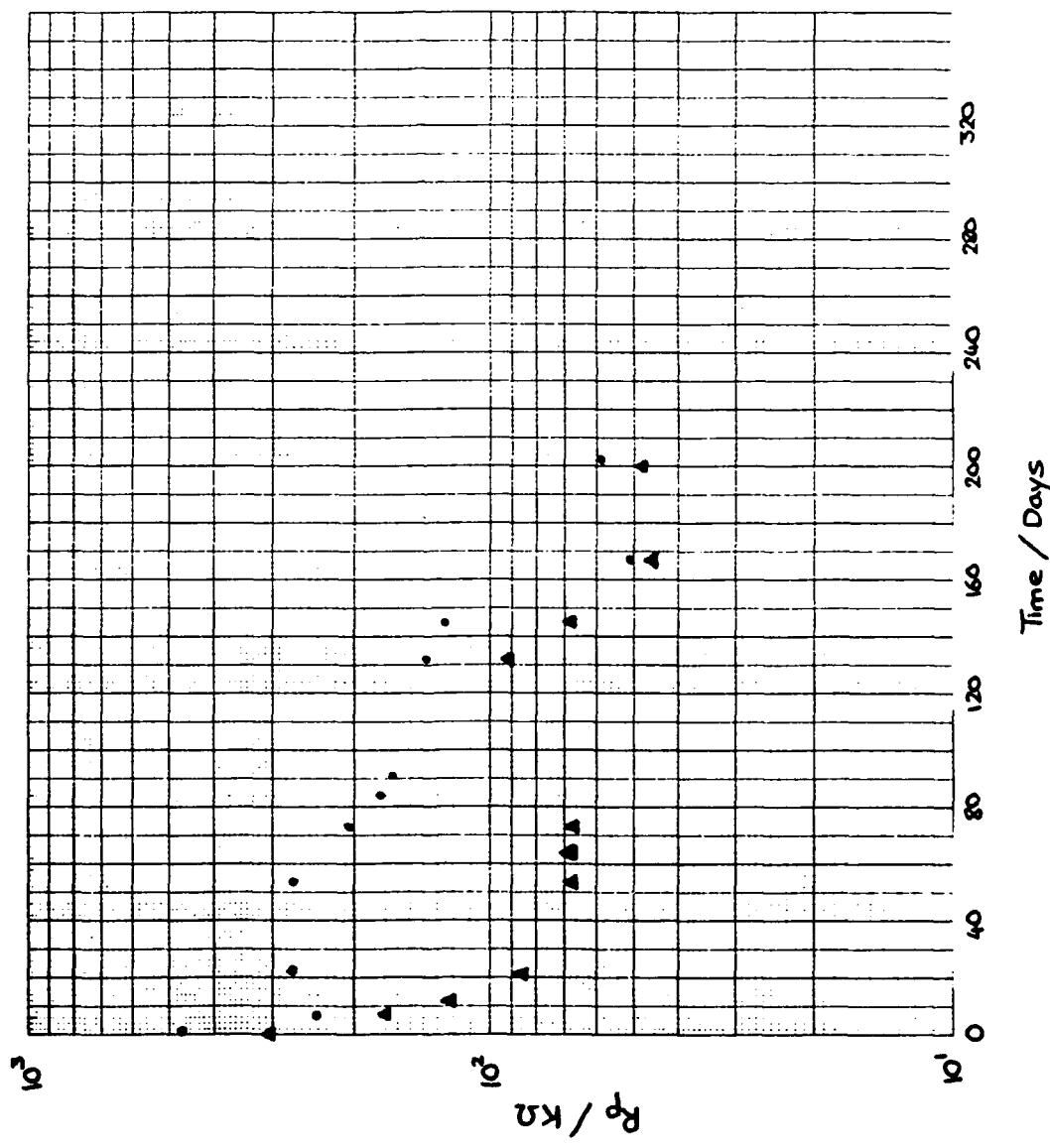


Figure 11
 R_p versus Time
SNS208/1 (○)
SNS208/2 (▲)

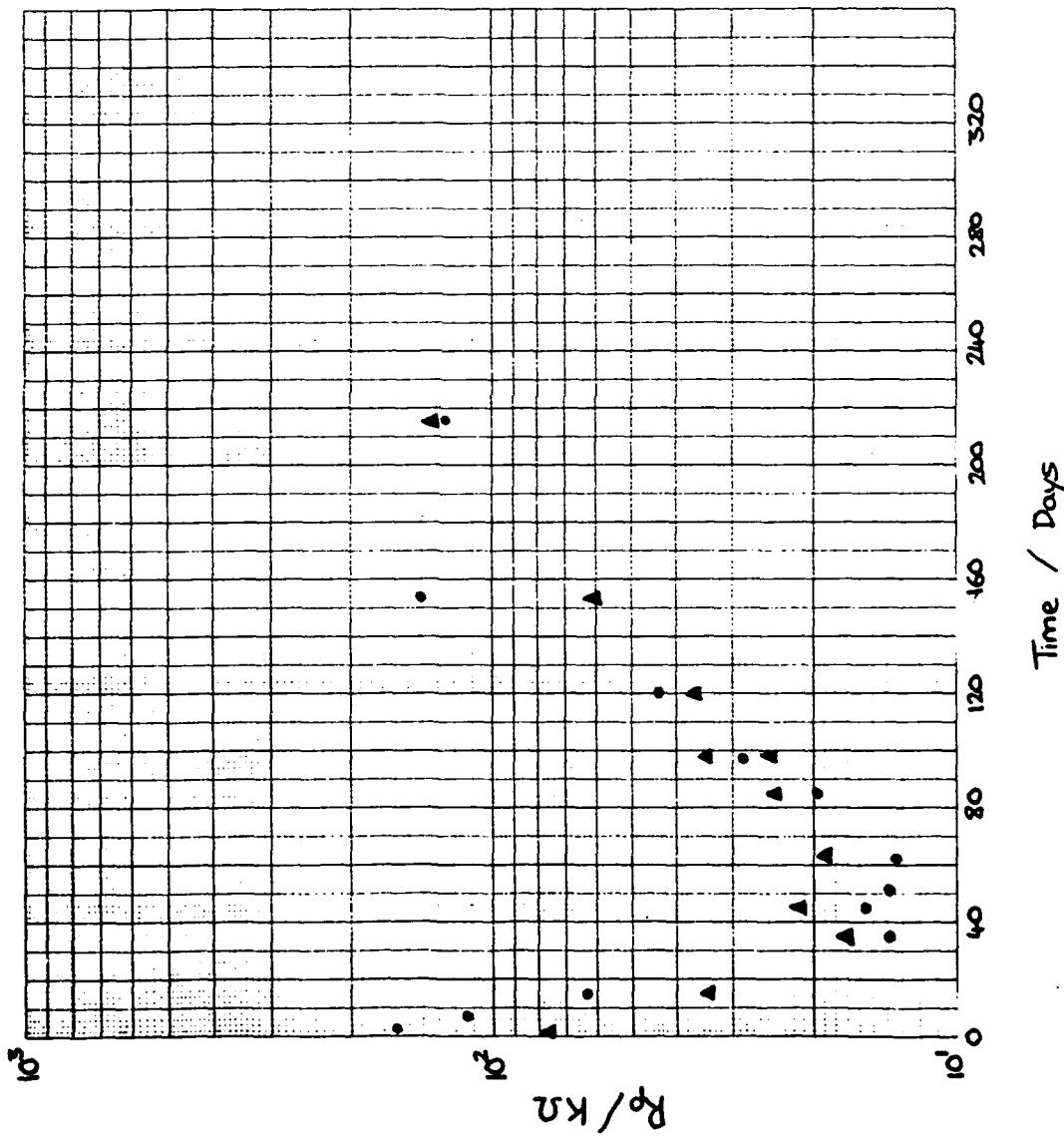


Figure 12
 R_p versus Time
W1 (•)
W2 (▲)

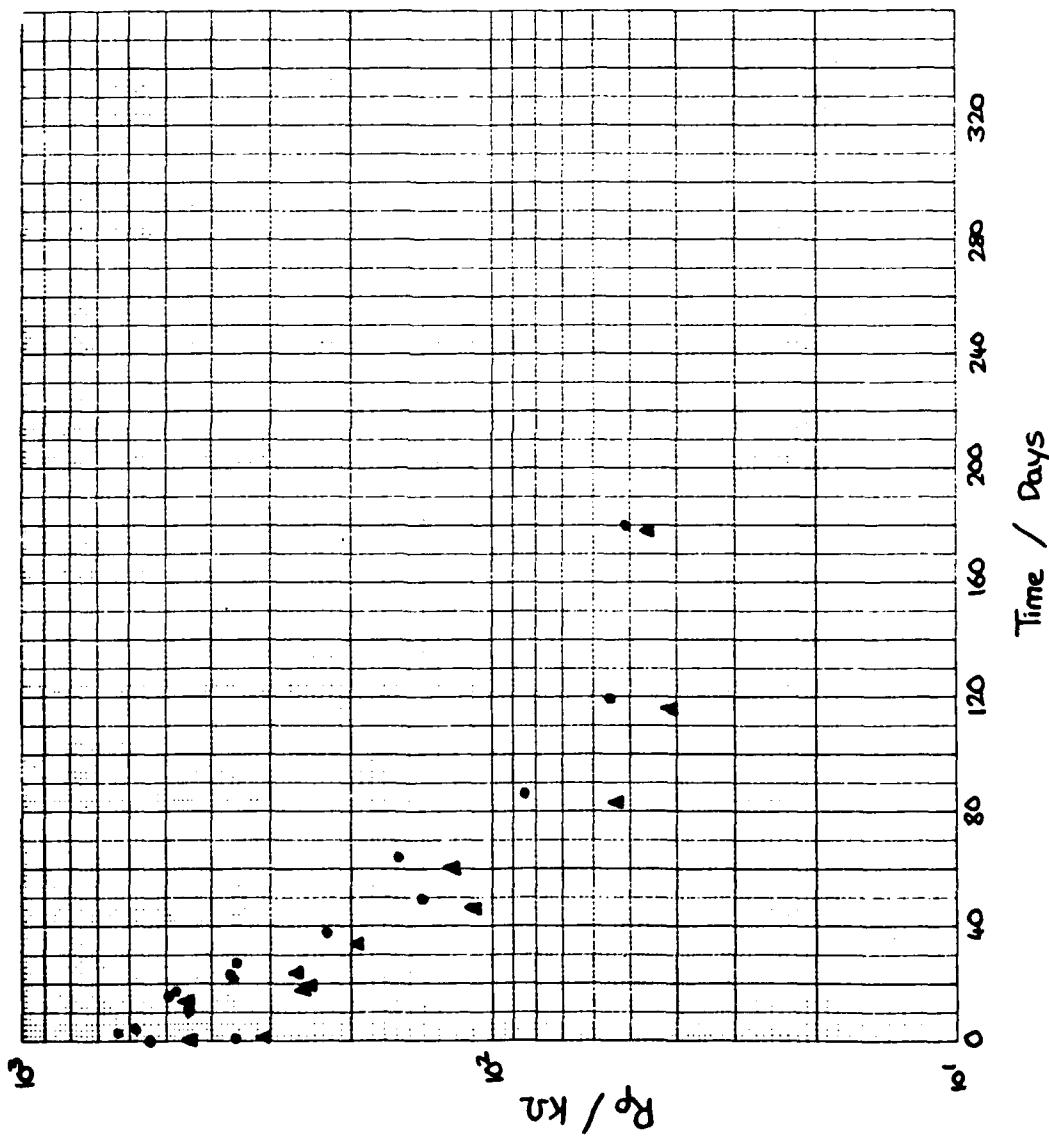
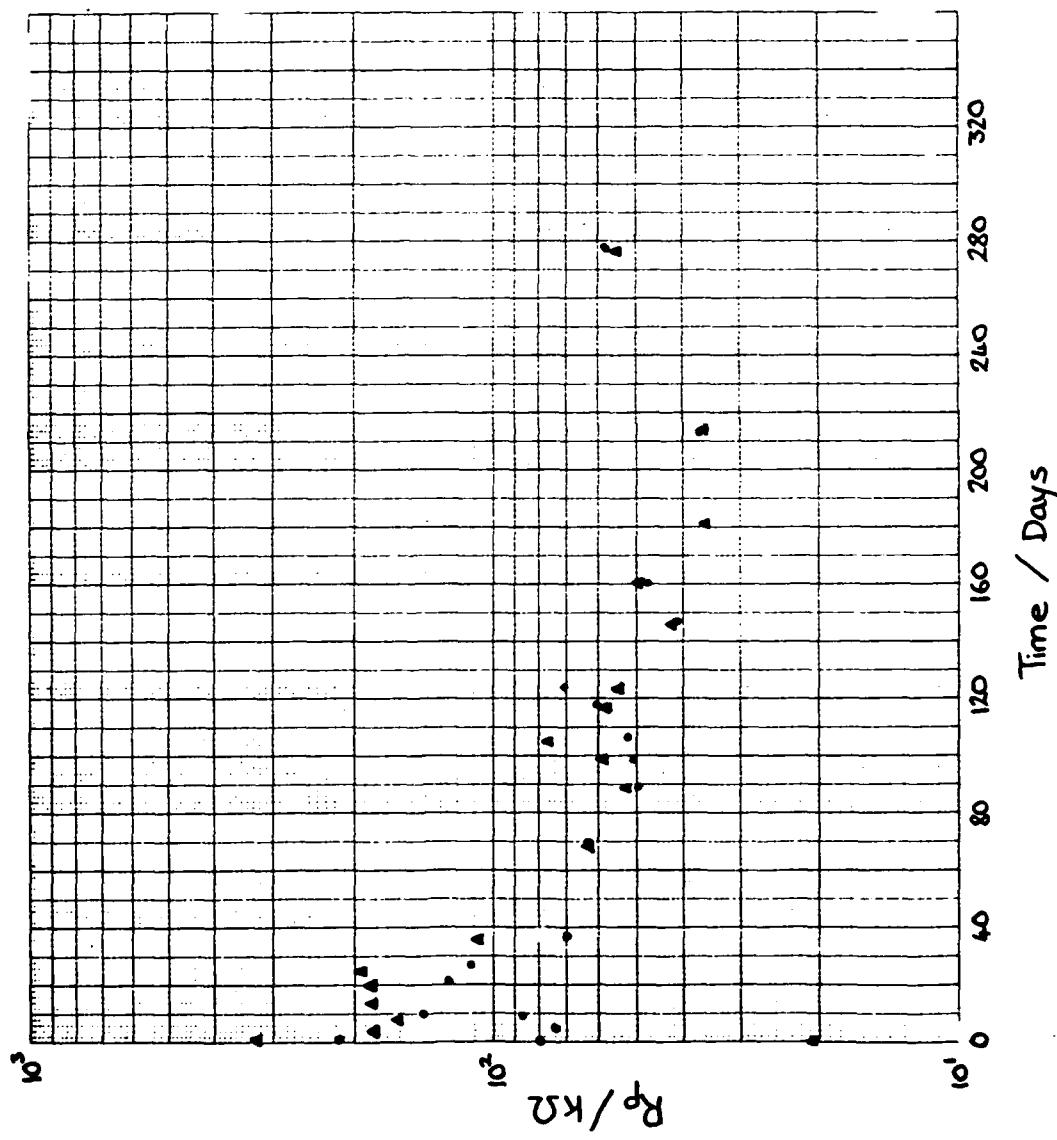


Figure 13
 R_p versus Time
Boom 1 (○)
Boom 2 (▲)



R_t -time behaviour is not reflected in E_{corr} -time behaviour (Section 4.2.1).

The results obtained from AF058/1 (Figure 10) show a lower rate of fall of R_t than for the other cells. However, after ca. 166 days, the value of R_t recorded (51 k Ω), is similar to results obtained from the other cells.

4.2.3) Dismantled Cells - Visual Inspection

The dismantling procedure for each cell was identical. The cell lid was removed under a stream of dry nitrogen, and the electrolyte removed (FEP pipette) to a storage bottle (FEP, screw-capped). Residual nitric acid/ N_2O_4 was removed by directing a stream of dry nitrogen into the cell interior. As the drying process proceeded, solid deposits became visible. The appearance of these deposits is reported in Table 4.2:

Table 4.2: The Appearance of Solid Residues

<u>Cell Code</u>	<u>Observations</u>
SN5208/1	Two types of solid visible. 1) White, flaky material on the working electrode surface. Quite thickly deposited. 2) Pale yellowish solid present on the cell walls.
SN5208/2	Thick, white, flaky deposit on the working electrode surface. Cell walls covered in a very thin layer of white, flaky solid.
Boom 1	White, flaky solid. Present on all surfaces as a thin deposit.
Boom 2	Same as Boom 1.
W1	White/pale green solid of powdery texture present as a thin film on all surfaces.
W2	White/green solid. Present on all surfaces as a thin layer.

4.2.4) Analytical Results

At the end of the testing period, the electrochemical cells were taken off test and dismantled. The acid electrolyte was recovered and analyses^a to determine water content and HF content were performed. The results are presented below in Table 4.3.

Table 4.3: HF and H₂O content of recovered IRFNA

<u>Cell code</u>	<u>[H₂O]/wt%</u>	<u>[HF]/wt%</u>
SN5208/1	6.45	0.119
SN5208/2	6.45	0.172
Boom 1	4.58	0.270
Boom 2	4.34	0.325
W1	4.19	0.367
W2	4.56	0.342
AF058/1	3.08	0.355
AF058/2	3.50*	0.401

* After addition of Cu²⁺ ions (Section 2)

In view of the fact that solid material recovered from cells W1 and W2 had a green colouration, qualitative (ammonium thiocyanate solution) tests for iron were carried out on the solid

material recovered from each of the electrochemical cells.

Solids recovered from cells W1 and W2 produced deep red colourations on treatment with thiocyanate solution, indicating the presence of Fe^{3+} ions. Samples of the solids from the Boom pair of cells gave a faint orange colouration. This probably indicates a low level of Fe^{3+} ions, since the deep-red coloured iron-thiocyanate complex is decolourised by the presence of fluoride ions.

Solids recovered from the SN5208 pair of cells gave a negative thiocyanate test result.

Since no solids were recovered from the AF058 pair of cells, no data is available concerning iron content.

4.3) Conclusions

The results of polarisation experiments carried out on four pairs of electrochemical cells are displayed graphically in Figures 10, 11, 12 and 13. These results indicate that 2014 (3L65) aluminium alloy corrodes at a similar rate in IRFNA obtained from three different sources (AF058, Wescott Lot67/Drum3 and Boom). In IRFNA obtained from these sources, the aluminium alloy shows a decrease in polarisation resistance with time, corresponding to an increase in corrosion rate. This effect is shown to occur for the first ca. 110 to 170 days of a cell lifetime. After this period, the polarisation resistance appears to achieve a minimum value (Figures 10, 12 and 13) of between 36 and 51 $k\Omega$ (63.6 and

90.1 $\text{k}\Omega\text{cm}^2$). There is some evidence that the polarisation resistance begins to increase after this minimum is reached (Figure 13).

The corrosion of 2014 (3L65) aluminium alloy in SN5208 IRFNA differs from the behaviour described above for this alloy in AF058, Westcott Lot67/Drum3 and Boom IRFNA (Figure 11).

The polarisation resistance minima (13.5 to 17 $\text{k}\Omega$) observed for the 2014 (3L65)/SN5208 system (Figure 11) occurred at ca. 35 and 63 days. After this period, a sharp increase in polarisation resistance was observed, corresponding to a decrease in corrosion rate. At ca. 216 days, the polarisation resistance was measured as ca. 130 $\text{k}\Omega$ ($229\text{k}\Omega\text{ cm}^2$); an order of magnitude greater than the minimum value recorded.

The analytical data presented in Table 6.1 (Section 6) and Table 4.3, show that IRFNA used to fill the SN5208 pair of cells (4.45 wt% H_2O), and the IRFNA recovered from the SN5208 pair of cells (>6.45 wt% H_2O), contained water concentrations in excess of the maximum level recommended by the current specification⁸.

In Section 3, it was shown that the increase of water content to a calculated concentration of 6.75 wt% led to a ten-fold increase in the corrosion rate of the alloy under investigation, and the thickening of the film of corrosion products as measured by AC impedance.

In view of the fact that thick, solid deposits were observed on the surfaces of the working electrodes of the two SN5208 cells, it seems reasonable to propose that the growth of

these deposits corresponds to the increase in polarisation resistance, R_{p} , with time, observed for these cells (Figure 11), and that the thicker films present on the surfaces of the working electrodes of the SN5208 pair of cells, (compared to the films present on the working electrodes of the other cells), result from the high water content (4.45 wt%) of the SN5208 IRFNA.

Table 4.3 also shows that the fluoride ion concentration of electrolyte recovered from the SN5208 pair of cells (0.119 and 0.172 wt%) is lower than in electrolyte recovered from the other cells, indicating that fluoride ions have been removed from solution to become incorporated into corrosion products.

The qualitative tests for Fe^{2+} ions carried out on solid material recovered from dismantled cells, indicate that Fe^{2+} ions are incorporated into deposited films. Solids from W1 and W2 had a green colouration, and gave positive Fe^{2+} reactions. Mellor* reports the presence of a green iron(III) fluoride hydrate resulting from the corrosion of 321 stainless steel in standard high density acid (SHDA).

It is probable that the iron present in the films recovered from the aluminium alloy electrochemical cells arises from the presence of iron in the IRFNA (Section 6).

5) Surface Studies

5.1) Introduction

Samples of 2014 (3L65) aluminium alloy taken from an oxidiser tank wall section (SN5144) were characterised using the Auger electron spectroscopy (AES) facility at Loughborough Consultants Ltd.

5.2) Experimental

Five pairs of samples were analysed. The pretreatments used were:

- A) Untreated
- B) H₂O wash
- C) H₂O wash, IRFNA (3 months)
- D) H₂O wash, HF/F₂ (1atm, 24 hours)
- E) H₂O wash, HF/F₂ (1atm, 24 hours), IRFNA (3months)

The experimental parameters, of the Auger spectrometer, used to perform the analyses are listed in the report (AU/UON/3395) from Loughborough Consultants Ltd., a copy of which is appended.

5.3) Experimental Results

The samples all appeared patchy on the secondary electron imaging system (SEI) attached to the Auger spectrometer. The light and dark areas appeared to represent regions where corrosion products had been removed, or not removed, respectively. The analyses were performed in the light areas away from any flaky

corrosion products.

Unfortunately, no reliable surface or sub-surface information could be obtained from those samples which had undergone IRFNA treatment (Samples C and E). These samples were covered with a loose flaky layer of poorly-conducting corrosion products. This insulating overlayer led to sample charging and hence any quantification of the Auger spectra proved impossible. Other surface techniques (e.g. SEM) could possibly be used in order to estimate the film thickness present on these samples. Depth profiles have been obtained for the other samples (Figures 14-17).

The untreated tank wall section had a thick film present on the surface (Sample A1, Figure 14). Carbon was detected on the outer surface at a concentration of 17 atom% .

The film consisted of a mixture of aluminium oxide and fluoride species. The ratio of aluminium:oxygen:fluorine was calculated at each etch depth. These ratios (Table 5.1) showed little variation throughout the depth of film analysed (1 μ m), although the top one or two atom layers show a higher oxygen and fluorine content than subsequent layers. The aluminium levels seen are higher than those expected, assuming that the film consists of a mixture of Al_2O_3 and AlF_3 . The levels of aluminium found indicate that some elemental metal is also incorporated in the film. This is consistent with an intergranular mode of attack.

Figure 14
Surface composition
of Sample Al (Blank)
determined by AES

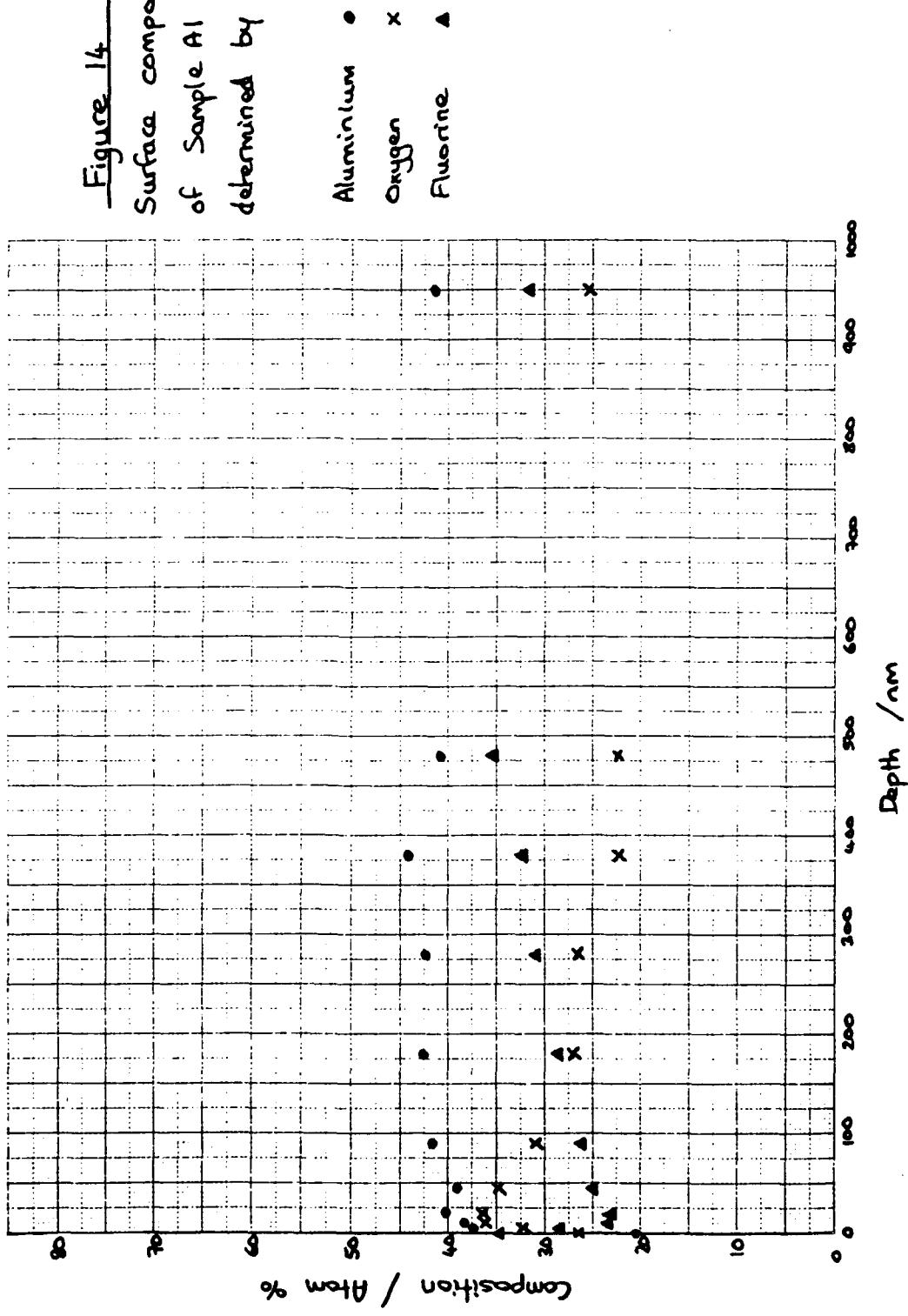


Figure 15
Surface composition of
Sample B1 - H_2O Wash, determined
by AES.

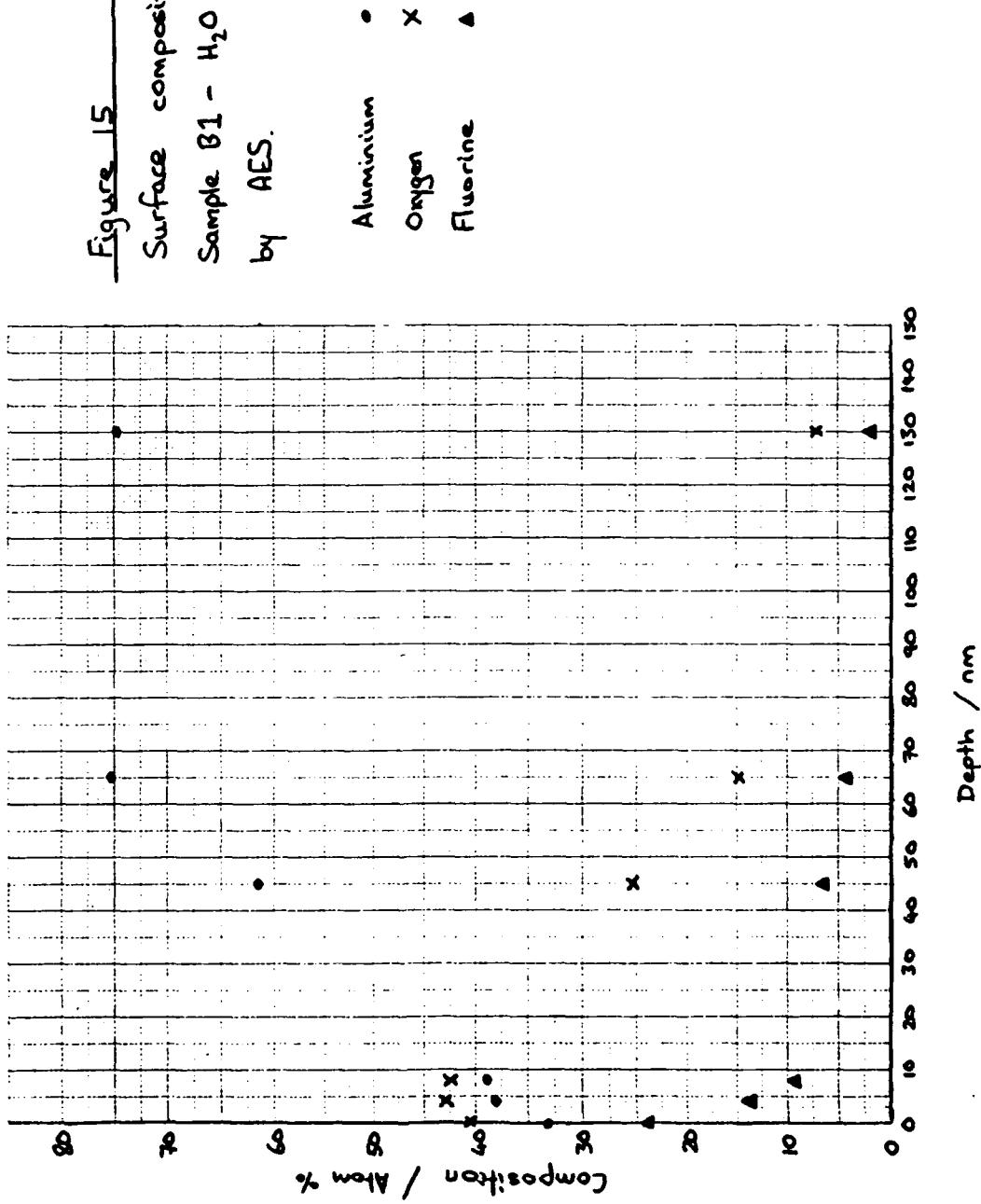


Figure 16
Surface composition of
Sample B2 - H₂O Wash,
determined by AES

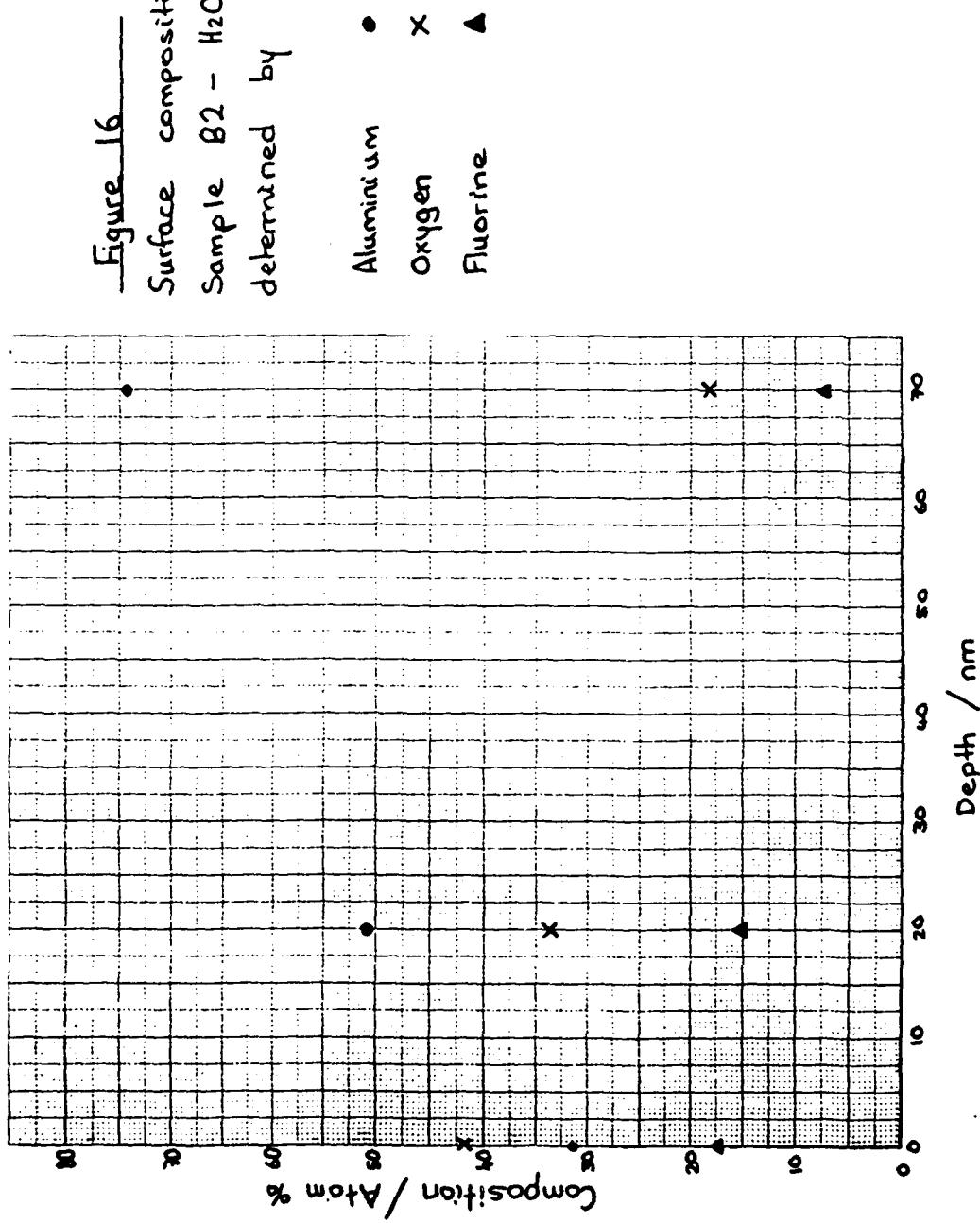


Figure 17
Surface composition
of Sample D1 -
 H_2O wash + HF/F_2 ,
determined by AES

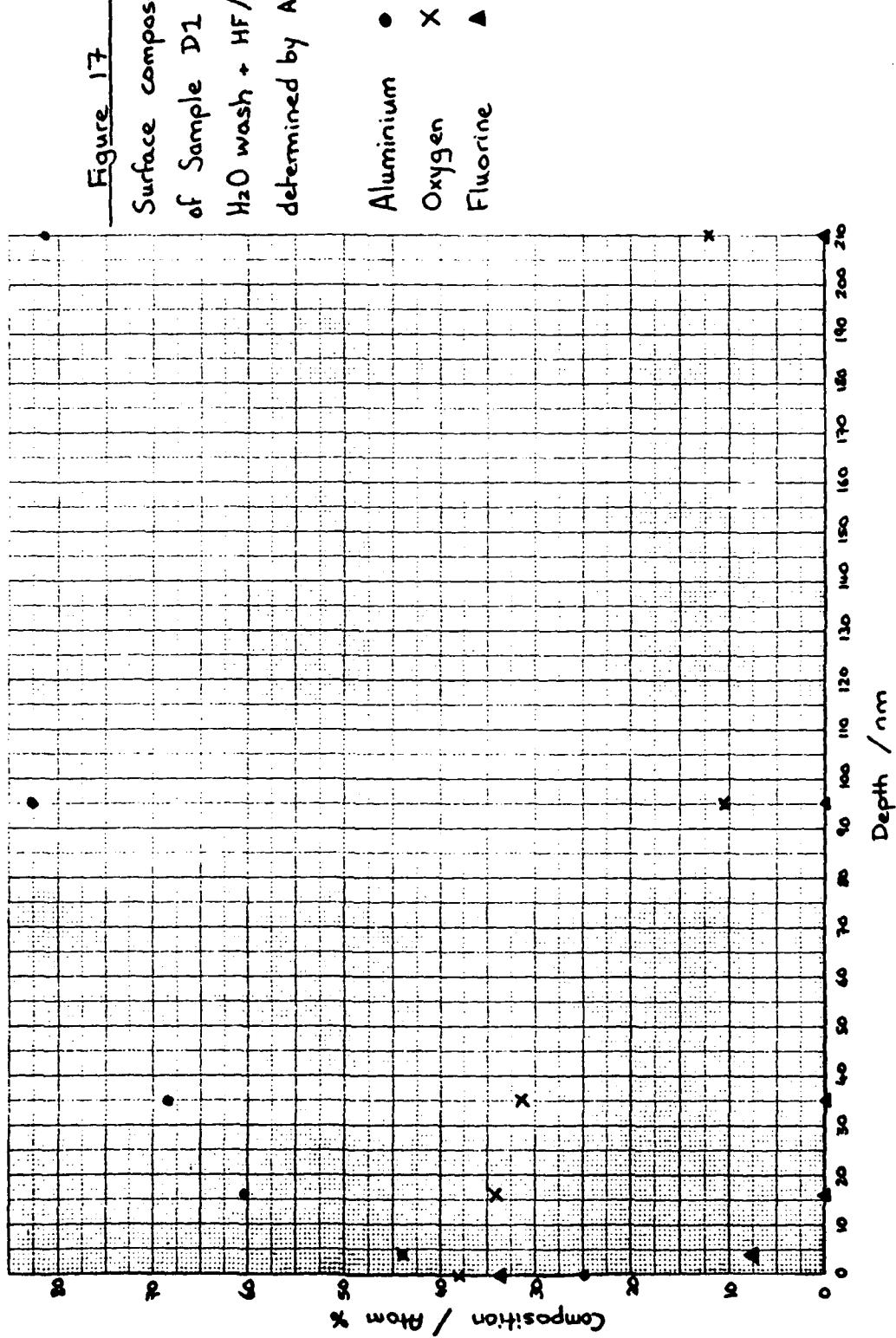


Table 5.1 Aluminium:Oxygen:Fluorine ratios for Sample A1

<u>Etch Depth / nm</u>	<u>Al:O:F</u>
0	1 : 1.29 : 1.69
5	1 : 0.86 : 0.76
10	1 : 0.95 : 0.58
20	1 : 0.90 : 0.58
45	1 : 0.90 : 0.60
90	1 : 0.74 : 0.63
180	1 : 0.63 : 0.67
280	1 : 0.63 : 0.73
380	1 : 0.51 : 0.73
480	1 : 0.55 : 0.87
950	1 : 0.61 : 0.76

Table 5.2 Aluminium:Oxygen:Fluorine ratios for Sample B1

<u>Etch Depth / nm</u>	<u>Al:O:F</u>
0	1 : 1.21 : 0.72
0	1 : 1.67 : 0.56
0	1 : 1.62 : 0.84
0	1 : 1.62 : 0.86
4	1 : 1.13 : 0.36
8	1 : 1.09 : 0.24
45	1 : 0.41 : 0.11
65	1 : 0.20 : 0.06
130	1 : 0.10 : 0.03

Table 5.3 Aluminium:Oxygen:Fluorine ratios for Sample B2

<u>Etch Depth / nm</u>	<u>Al:O:F</u>
0	1 : 1.33 : 0.55
0	1 : 1.99 : 1.51
20	1 : 0.66 : 0.30
70	1 : 0.25 : 0.10

Table 5.4 Aluminium:Oxygen:Fluorine ratios for Sample D1

<u>Etch Depth / nm</u>	<u>Al:O:F</u>
0	1 : 1.53 : 1.35
0	1 : 1.45 : 1.32
4	1 : 0.99 : 0.18
16	1 : 0.56 : 0
35	1 : 0.46 : 0
95	1 : 0.13 : 0
210	1 : 0.15 : 0

Analysis of the tank wall sections which had received a water wash (Samples B1, B2 and D1, Figures 15, 16 and 17 respectively) indicated that the film thickness was reduced by the water treatment. The aluminium:oxygen:fluorine ratios are presented in Tables 5.2, 5.3 and 5.4 respectively, and show that the films present on the surfaces of the washed samples have different compositions to both surface and bulk films present on the untreated sample (A1, Table 5.1).

The reduction in film thickness can be quantified in terms of half-film thicknesses (Table 5.5). The half-film thickness is defined as the depth at which the level of oxygen in the sample has fallen to half its surface value.

TABLE 5.5: Half Film Thicknesses

Sample	:	A1	B1	B2	D1
Half-Film Thickness	:	>1000nm	50nm	60nm	70nm

The effect of the water washing process is therefore seen to be the removal of a substantial part of the film of corrosion

products from the alloy surface.

The analysis of the sample which had been fluorinated (HF/F₂, 1atm., 24hrs, RT, Sample D1, Figure 17) indicated that the pretreatment has little effect on the surface or sub-surface composition of the sample. A slight enhancement of the fluorine content (about 10atom%) on the outer surface of the sample was observed. However, the enhancement of the fluorine content only persisted to a depth of about 4nm into the film.

5.4) Conclusions

The washing of the samples in water produced an appreciable decrease in the thickness of the layer of corrosion products present on the sample surface. The gaseous fluorination procedure however, has little effect on the composition and thickness of the film on the metal.

6) Analytical Results

The results of analyses carried out on the various batches of IRFNA used throughout this work are reported below in Table 6.1 (Metals content) and Table 6.2 (Water, HF and Total Dissolved Solids (TDS) content).

Metal contents were determined by atomic absorption spectrophotometry (AAS).

Total solids determinations were performed according to the method outlined in the U.S. Army laboratory analysis standard for IRFNA*, and water contents were determined from the near infra-red absorption spectrum of the sample between 1500 and 1350 μ (nm) versus CCl₄, both contained in 5mm path length cells as described in Ref.5.

Fluoride ion concentrations were determined using the specific fluoride ion electrode as reported previously in Reference 6.

Table 6.1: Metals Content of "Stock" IRFNA

IRFNA Source	Metal Concentration/wppm				
	Al	Fe	Cu	Cr	Ni
"New" Westcott	200.2	366.6	4.3	34.1	39.5
Westcott Lot67 Dr.3	101.5	90.2	1.8	34.9	31.2
SN5208	180.6	11.5	8.8	34.1	0.5
AF175	194.1	7.5	1.1	1.6	0.5
AF058	205.0	6.8	1.1	1.7	ND
Boom	147.6	6.5	7.0	0.9	0.4

ND = none detected

Table 6.2: Total Dissolved Solids (TDS), H₂O and HF content of "Stock" IRFNA

IRFNA Source	TDS / wt%	[H ₂ O] / wt%	[HF] / wt%
"New" Westcott	-	2.79	0.559
Westcott Lot67 Dr.3	0.14	2.75	0.55
SN5208	0.065	4.45	0.576
AF175	0.069	1.74	0.592
AF058	0.043	2.839	0.503
Boom	0.058	2.16	0.519

7) References

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